23rd ABCM International Congress of Mechanical Engineering
December 6-11, 2015, Rio de Janeiro, RJ, Brazil

INFLUENCE OF TEMPERATURE AND PARTICLE SIZES ON THE FIXED BED PYROLYSIS OF SOLID GRAPEFRUIT WASTE

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Abstract. *This work were carried out studies pyrolysis fixed bed reactor of solid grapefruit waste to heating rate of 10 ºC/min, different final pyrolysis temperatures between 300 and 900 ºC and particle sizes less than 300 μm and between 300 and 800 μm. The 2^k full factorial design is used, evaluating the influence of the independent variables and their interactions in the product yields (char, tar, and gas), Lower heating value of gases, gas density, and the contents of individual gases, using an analysis of variance and a degree of significance of 95 %. Conditions for realization the process are determined and the results demonstrate that increasing the temperature decreases the char yield to about 12 %, increase the gas yield in 7 % for the 300 < Tp < 800 μm and 2 for Tp < 300 μm. To increase the char yield in pyrolysis fixed bed reactor is obtained whit to heating rate of 10 ºC/min, a temperature of 400 ºC and a particle size of 300-800 μm.*

Keywords: *pyrolysis, temperature, particle sizes, grapefruit*

1. INTRODUCTION

Renewables energies are part of a worldwide strategy involving the scientific community, with the purpose of finding ways of energy use that could be in the near future oil substitute. While it is true that petroleum is unsurpassed in its features, versatility, heating value and extensive use of derivatives, is detractor its high contamination to the atmosphere. Biomass as a renewable energy and sustainable event offers the possibility of generating energy, chemicals product and coal through thermochemical processes used today such as pyrolysis and gasification.

The citrus processing industry generates a high volume of waste. The application of new technologies can used these residues, reduce and contribute to the development of new works in the field of utilization of industrial waste as fuel, in line with the policies of the countries in the development of renewable energy (Suarez 2012). The alternative of using pyrolysis as a process capable of providing an easy, viable, economic and foreign energy solution to pollution dates back many years.

In Cuba citrus company, it is working with different varieties of fruit such as grapefruit, orange and lemon, obtaining juice, concentrated juices, essential oil and generating high volume of solid waste. These residues have been used as animal feed and other purposes, but it is necessary to transport and greatly affects not only the establishment but also those who provide transportation service.

The objective is to determine, on a laboratory scale by slow pyrolysis process, the usability of solid grapefruit waste (GW) for energy analyzing the influence of temperature and the particle size of the waste.

2. EXPERIMENTAL PROCESS

2.1 Feedstock

The raw materials used are solid grapefruit waste (GW), which is mainly composed of grapefruit husk or peel and seeds. Treatment processes used were drying until a moisture content of 8 %.

2.2 Analysis in the solid grapefruit waste

The proximate analysis was performed at the University of Pinar del Rio and the results are shown in Table 1. With the results of proximate analysis, was determined the elemental analysis (Table 2), from the equations referenced by Jigisha 2007 and the heating value of the waste was determined using the formulas proposed by Dulong, Table 3, Nzihou 2014.

Table 1. Proximate analysis of GW (weight %).

Parameter	**Analytical Norma**	**Dry**
Ask (%)	ASTM E 1755-01	4,41
Volatile matter [VM] (%)	ISO-5623-1974	83,47
Fixed Carbon [FC] (%)	by difference	12,12

Table 2 Ultimate analysis of GW (weight %).

Carbon (C) (%)	C = 0,637·FC + 0,445·VM	45,69
Hydrogen (H) (%)	H = 0,052·FC + 0,062·VM	5,80
Oxygen (O) (%)	O = 0,304·FC + 0,476·VM	43,41
Nitrogen (N) (%)	By difference	5,11

Tabla 3: Higher heating value (HHV) and lower heating value (LHV) of **GW**.

Properties	**Equations**	**Dry base**
HHV (kJ/kg)	$HHV_{Biomasa} = 337{,}3(C) + 1418{,}9\left[H - \left(O/8\right)\right] + 23{,}3(N)$	16327
LHV (kJ/kg)	$LHV_{Biomasa} = HHV_{Biomasa} - 25\left[9\left(H - O/8 + \%\ Moisture\right)\right]$	14450

2.3 Installation experimental

The pyrolysis runs were performed in a bench scale plant, shown in Figure 1, consisting of a fixed bed reactor, discontinuous for the solid feed. The reactor is inside a tubular electric furnace, connected to a temperature and heating control system. Computer software provides a continuous record of carrier gas flowrate, time and temperature of the furnace.

A steel basket containing a sample weight of 40 g.

Once the reactor is closed, a nitrogen flow of 800 mLNTP/min (NTP: normal temperature and pressure, 0 ºC and 1 atm) is set by means of a mass flow controller. After 30 min under nitrogen flow, when the air is purged from the reactor, heating of the sample starts at the selected heating rate from 10 ºC/min until the final pyrolysis temperature is reached. The temperature of the reactor is then kept constant for 90 min to make sure that the pyrolysis process is complete.

The exit gas passes through a tar condensation system which consists of two glass condenser vessels cooled with a mixture of ice and water and an electrostatic precipitator. The clean gas is analyzed by GC-TCD, by an on-line micro gas chromatograph Agilent 3000A. The compounds analyzed are H_2, N_2, CH_4, CO, CO_2, C_2H_6, C_2H_4, C_2H_2 and H_2S. Once the experiment is finished and the system is cooled down to room temperature, the char is removed from the basket and weighed. The tar collected by the tar condenser system is also weighed and subsequently extracted with 2-propanol. Water content is analyzed by Karl–Fischer titration , Oasmaa 2005.

From one experiment the weight of char and tar are measured, as well as the gas composition. From these data, the following responses were considered:

a) Product distribution, as the weight percentage of each fraction: char (Ychar), gas (Ygas), tar (Ytar) and water (Ywater).
b) Average gas composition and lower heating value of the gas, LHVg.
c) Higher heating value of the char (HHVchar). This value was estimated using the method proposed for Cordero et al 2001 from data of volatile matter and fixed carbon. These data were determined for each char obtained using the methods proposed in standards UNE 32-004-84 for ash, ISO 562-1974(F) for volatile matter. Fixed carbon was calculated by difference.

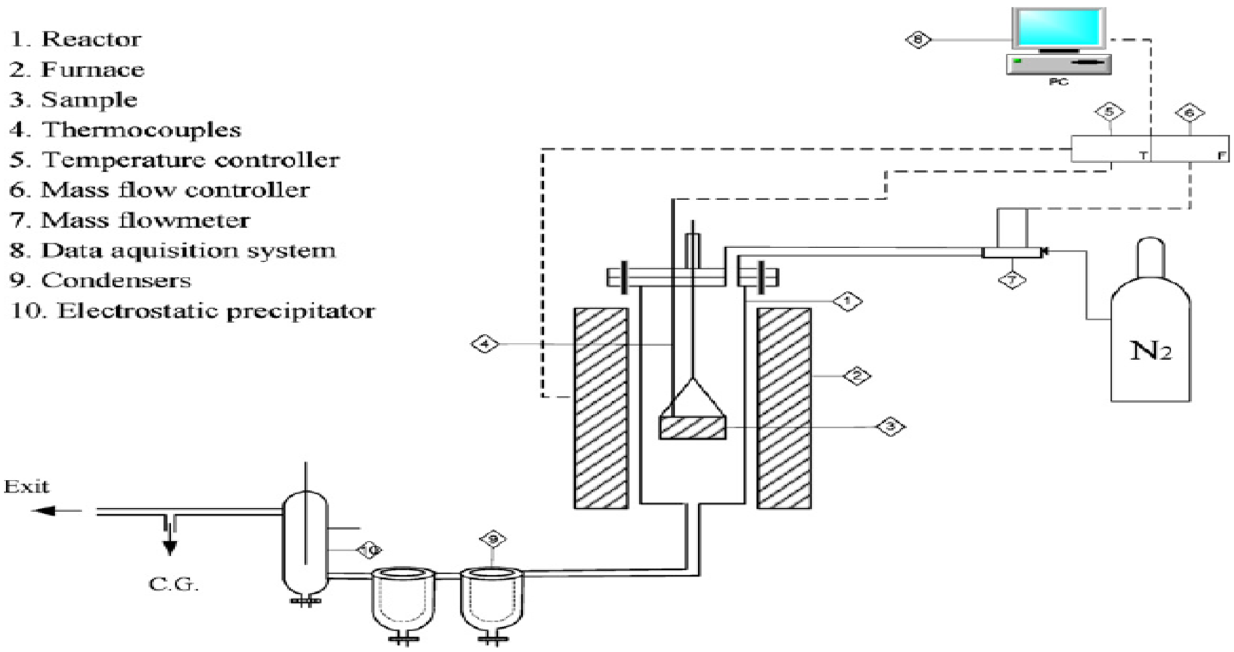

Figure 1: Experimental System

2.4 Design of Experiment

It was used a full factorial design. The only two varied factors are final pyrolysis temperature (T) and the average particle size (Tp) of the grapefruit husk used. The temperature range chosen for this study was 300 – 600 ºC, whereas two particle diameter ranges were used, the fractions smaller than 300 µm and between (300 – 800) µm. An experimental design setup of two factors and two levels for each factor were used (namely 2^k), adding a central point for the temperature (450 ºC). The central point was replicated six times, which leads to 10 experiments. The order in which the experiments was carried randomly in order to avoid the effect of external or uncontrolled factors.

Analysis of variance (ANOVA) was used to study the influence of temperature, particle size, and their possible interaction on the results obtained. The ANOVA method was developed as a way to interpret results from experiments where different factors were

varied. In this method, the variance observed in the results is decomposed in different fractions that can be assigned to the influence on those results (gas composition, production, etc.) of the different factors studied (temperature and particle size). Thus, the

information from all the experiments is used in the analysis of the results, making ANOVA a more powerful tool than varying only one factor at a time. By repeating the experiments, the influence of non-controlled factors (such as the effect of ambient conditions), can also be determined as the error of the results. A detailed explanation of the ANOVA method can be found elsewhere, Montgomery 2005.

The statistical analysis was carried out using the Design-Expert 7, Software from Stat-Ease, Inc. To consider a given significant effect (to reject the null hypothesis that changing the factor has no effect on the observed response), a confidence level of 95 % for the F-distribution was selected.

3. RESULTS AND DISCUSSION

Results obtained in the experiments performed are shown in the table 4 and 5

Table 4. Product distribution (char, gas, tar and water), and gas and char heating values.

T (ºC)	Tp (µm)	Ychar (%)	Ygas (%)	Ywater (%)	Ytar (%)	LHV_{gas} (kJ/m^3N)	HHVchar (kJ/kg)
300	300-800	38,8	21,51	31,12	3,45	970,8	25410
300	-300	38,55	21,51	33,4	4,75	911,02	25011
450	300-800	29,38	23,79	37,61	3,34	900,97	28170
450	-300	28,4	22,21	35,17	7,55	374,5	27251
450	300-800	29,37	23,63	37,64	3,34	930,94	28111
450	-300	28,18	21,9	34,24	6,26	587,46	27310
450	300-800	29,38	23,71	37,63	3,34	915,96	28140
450	-300	28,29	22,56	34,71	6,91	530,98	27280
600	-300	26,53	23,39	33,52	8,31	347,58	28262
600	300-800	26,8	28,55	38,32	3,23	1777,2	29010

Table 5: Gas distribution

T (ºC)	450	600	450	300	450	300	450	600	450	450
Tp (µm)	300-800	-300	-300	300-800	-300	-300	300-800	300-800	300-800	-300
H_2 (%)	0,59	3,41	0,92	0,59	0,57	0,54	0,59	4,21	0,58	0,75
CO (%)	1,77	2,46	2,73	1,96	1,83	2,07	1,78	3,06	1,78	2,28
CH_4 (%)	1,12	1,62	1,41	1,15	1,02	1,21	1,14	1,95	1,15	1,22
CO_2 (%)	4,72	4,54	4,52	4,67	4,09	5,17	4,73	4,66	4,73	4,31
C_2H_4 (%)	0,1	0,13	0,1	0,08	0,07	0,08	0,15	0,15	0,20	0,09
C_2H_6 (%)	0,2	0,19	0,18	0,15	0,13	0,16	0,2	0,20	0,20	0,16
C_2H_2 (%)	0,03	0,04	0,04	0,01	0,01	0,01	0,04	0,04	0,04	0,03
H_2S (%)	0,09	0,1	0,1	0,06	0,07	0,07	0,07	0,10	0,10	0,08

In Table 6 the relative influence of each factor (temperature and particle size) is shown, as the result of the ANOVA analysis

Table 6: Relative influence of the temperature and particle size on the product distribution

	Ychar	Ygas	Ywater	Ytar	LHV_{gas}	HHVchar	H_2	CO	CH_4	CO_2	C_2H_4	C_2H_6	C_2H_2	H_2S
T	-, *	+, *	+, *	+	+	+, *	+, *	+	+, *	-	+	+	+	+
Tp	+	+	+	-	+, *	+	+	+	+	-	+	+	+	-
T-Tp	-	+	+, *	-	+, *	+	+	+	+	+	+	+	+	+

+ Positive Effect on the product with increasing parameter
-, Negative Effect on the product with increasing parameter
***, significant influence on the product**

3.1 Effect of pyrolysis temperature and particle size on the pyrolysis process.

3.1.1 Char Yield (Ychar)

The ANOVA of the results show, table 6, that char yield decrease as temperature increases and product at interaction T-Tp and increases as particle size of the waste sample increases, the temperature is the only parameter that has significant influence in the process. As can be observed in figure 2, this behavior. Similar tendencies have been observed for Aguiar 2008; Ayllón 2006; Demirbas 2004, 2006; Haykiri-Acma 2006; Tsai, 2006.

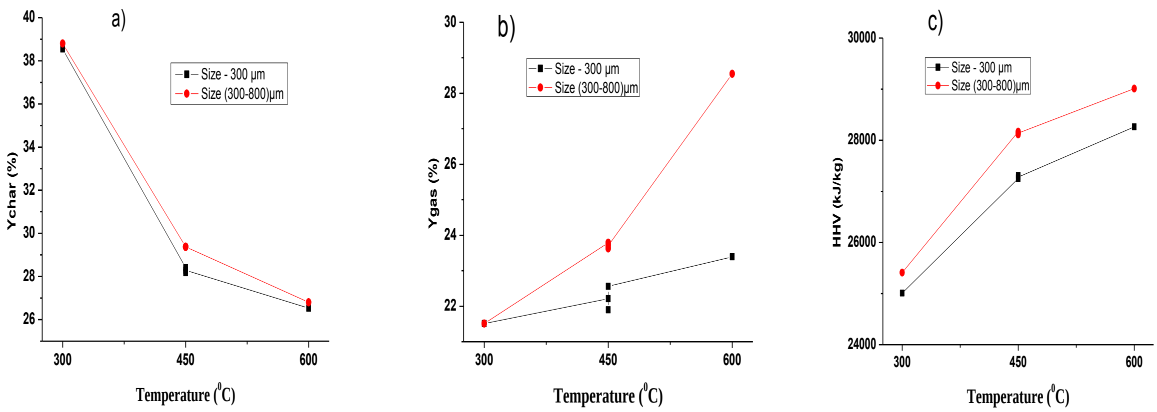

Figure 2: Product distribution: a) Ychar, b) Ygas and c) HHVchar

3.1.2 Gas yield (Ygas)

The gas yield, is shown in Figure 2, the ANOVA analysis, table 6, shows that the particle size of the waste and the interaction T-Tp does not have a significant influence, only the temperature. All parameters, T, Tp and interaction T-Tp increase of gas yield. This tendency was also observed in the previously cited works Özbay, 2008; Encinar 1996; Strezov, 2007; Apaydin-Varol, 2007; Ayllón 2006; Aguiar 2008.

3.1.3 Higher heating value (HHVchar)

The higher heating value of the char, is shown figure 2, increases with increasing temperature, the particle size and the interaction product, due to higher fixed carbon in the char obtained with increasing temperature. The ANOVA analysis, table 6, shows that the temperature is the only parameter that has significant influence in the process. Similar behaviors are obtained by Mesa-Pérez 2005; Demirbas 2006; Maiti, 2006.

3.1.4 Gas distribution

In the pyrolysis process, cracking gases occurs breaking bonds obtaining higher decomposing hydrocarbon molecules into smaller molecules

Low temperatures promote the production of a gas rich in CO_2, C_2 and high gas temperatures provide a significant concentrations of H_2, CH_4 and CO, figure 3. Similar tendencies have been observed for Aguiar 2008, Pütün 2005, Encinar 2000.

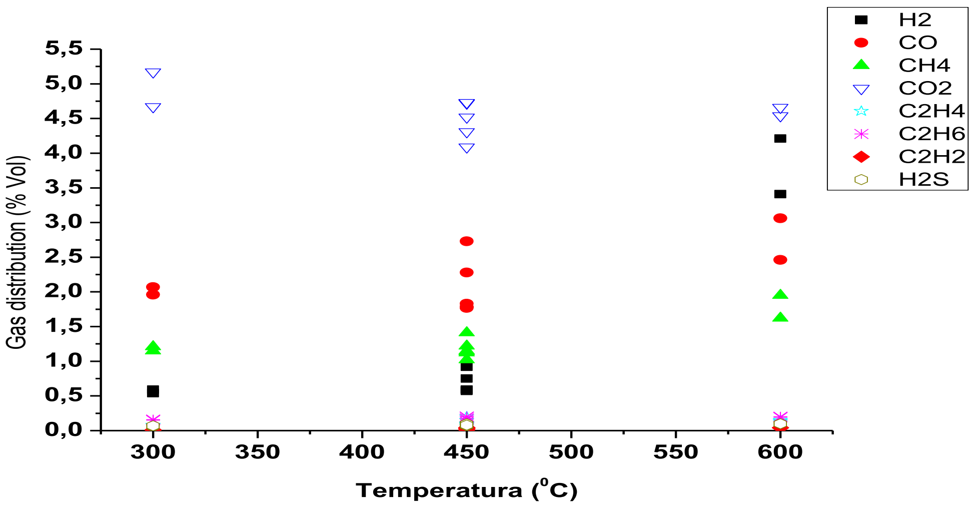

Figure 3: Gas distribution

The ANOVA analysis, table 6, shows that the temperature is the only parameter that has significant influence in the formation of H_2 and CH_4, in the other gases have not significant influence. The particle size and interaction T-Tp not significant influence on the formation of gases.

The energetic use of char obtained in the process of slow pyrolysis requirement a high char yield and higher heating value. Maximizing the char yield and higher heating value of char and minimizing tar yield, according to analysis of variance and confidence level of 95 %, the conditions which must be taken slow pyrolysis in fixed bed reactor are heating rate 10 ºC/min, T = 400 ºC and Tp = 300 – 800 μm.

4. CONCLUSIONS

- In the slow pyrolysis process range considered (temperature, (300 – 600) ºC; particle size, Tp < 300 µm, 300 < Tp < 800 µm), pyrolysis temperature exerts a more significant effect than particle size in the parameters analyzed and had significant influence on the Ychar, Ygas, Ywater, HHVchar, H_2, CH_4.
- An increase of the temperature reduces the char yield (about 12 % from 300 to 600 ºC) but increases its higher heating value (among 3200 and 3600 kJ/kg in this temperature range).
- An increase of the temperature increase de gas yield in 7 % for the 300 < Tp < 800 μm and 2 % for Tp < 300 μm.
- The particle size and the interaction (T-Tp) only had significant influence on the LHV, increasing LHV value analyzed at each temperature, the increase being higher for 600 ºC.
- The energetic use of char obtained in the process of slow pyrolysis in fixed bed reactor is obtained whit to heating rate of 10 ºC/min, a temperature of 400 ºC and a particle size of 300-800 μm

5. ACKNOWLEDGEMENTS

The authors express their gratitude to the E.C. for financial support under Alpha Program II (Contract No. AML/B7-311/97/0666/II-0444-FA) and Desarrollo de una planta de gasificación de fangos y compost, número 2006/572, Zaragoza University, Spain, for the grant awarded to Leonardo Aguiar Trujillo.

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